

- 1 -

GLASS PLATE INTENDED TO RECEIVE A METAL COATING AND
RESISTANT TO COLORATION LIABLE TO BE CAUSED BY SUCH A
COATING

5 The present invention relates to a glass plate intended
to constitute a plate-shaped product provided on at
least part of at least one of its faces with a metal
coating, the said plate being resistant to coloration
due to at least one metal species M^{n+} of the said metal
10 coating, which species, under the conditions in which
the product is manufactured and/or used, would be
liable to migrate into the glass from its surface and
then undergo reduction to the species M^0 responsible
for the coloration.

15 The metal species that may induce undesirable
coloration are in particular Ag, Cu and Au.

Such undesirable colorations appear, owing to
20 interactions between the components of the glass and
these metal species, either during manufacturing
treatments carried out on the products, more
particularly when these treatments include heating
steps that encourage the migration of the species
25 responsible for the undesirable coloration in the
glass, and also throughout the ageing and use of the
products, in particular when the use involves a high
temperature and/or electron bombardment.

30 The plate-shaped products having received a metal
coating that are subject to the risks of glass
coloration are called "substrates" in the electronics
field. These are for example the faceplates of
television screens and computer screens, and, in
35 general, emissive displays, such as plasma display
panels, electroluminescent displays and cold-cathode or
field-emission displays.

As other products, mention may be made of flat lamps,

index-graded microlenses and heated rear windows for motor vehicles.

Current emissive displays comprise a glass substrate on which very thin transparent layers of mixed indium tin oxide (ITO) have been deposited, followed by very thin, and also transparent, silver layers constituting a second array of electrodes, these electrodes lying within a dielectric.

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It has been observed that these substrates have a tendency to develop a yellow coloration, which contributes to degrading the image quality, especially by reducing its luminous intensity and by modifying its colours, and which gives the display a dirty and not very presentable appearance. This yellowing phenomenon is attributed to the fact that the Ag^+ ions migrate into the glass, where they are reduced to the form of colloidal Ag^0 particles, which absorb light within the wavelength range from 390 to 420 nm.

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This coloration anomaly may appear at various times:

- during manufacture of the display, if it was necessary to carry out a high-temperature treatment, the rise in temperature encouraging the migration of Ag^+ ions;

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- during use for example, when the temperature rise or electron bombardment will further encourage coloration; and

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- by normal ageing of the display, the Ag^+ ions migrating further over the course of time, especially when a voltage is applied.

The same problems as with displays arise with flat lamps, microlenses and rear windows.

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There is therefore a need to have a glass plate as defined above that does not suffer coloration under the conditions in which the final products, such as

displays, are manufactured and used.

The present invention provides a solution to this problem.

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For this purpose, the glass plate according to the present invention is characterized by the fact that it includes, at least on the surface and on at least one face sensitive to coloration, a composition capable of limiting or preventing the said migration and/or the said reduction of the one or more M^{n+} species.

15 In accordance with one particular feature of the glass plate according to the present invention, the said plate may thus be produced so as to present, on the surface and on the face or faces sensitive to coloration and at least over a depth to which the M^{n+} species is capable of migrating, a quantity of reducing agent capable of reducing the M^{n+} species, this quantity being at most equal to 1.40×10^{-7} mol/cm², in particular at most equal to 7×10^{-8} mol/cm² and advantageously at most equal to 3.5×10^{-8} mol/cm² when the M^{n+} metal species is Ag^+ .

25 The reducing agent is chosen from elements having several oxidation states, such as Fe, S, Sn, Sb and mixtures of these elements. It is preferred to choose Fe, S and/or Sn.

30 The protocol for this measurement is given below.

A metallic silver layer about 400 nm in thickness is deposited on the glass sheet by cathode sputtering. Next, the sheet is heated in air for one hour at 600°C then treated with nitric acid so as to remove the surface silver layer.

The profile of the silver in the subsurface layer of the glass is measured by SIMS: the profile has a peak

corresponding to the reduction of the silver by the reducing agent. The amount of reducing agent, in mols per cm^2 , is obtained by measuring the silver content integrated over the thickness of the glass
5 corresponding to the silver peak.

This measurement expresses the quantity of reducing agent on the surface of the glass that must not be exceeded, so that the M^{n+} ions cannot be reduced to the
10 point of inducing unacceptable coloration. A glass obtained by the float process has, on its face in contact with the bath of molten tin, a higher content of reducing agent than on the opposite face. However, it would not be enough merely to apply the layer
15 containing the metal liable to migrate onto this second, less coloration-sensitive, face.

It should also be mentioned that the said quantity of reducing agent according to the invention is that of
20 the glass as produced without an additional polishing step that would allow the surface layer having the desired quantity of reducing agent to be reached.

In accordance with another particular feature of the
25 glass plate according to the present invention, the said plate is provided, on the coloration-sensitive face or faces, with a layer acting as a barrier to the migration of the M^{n+} species, to which barrier layer continuous or discontinuous functional layers are
30 capable of adhering, and which barrier layer is unable to react chemically with the said functional layers so as to degrade the properties thereof.

In particular, the barrier layer may be chosen from
35 layers based on one or more metal oxides, such as SiO_xC_y ($x = 0-2$; $y = 0-1$, the limits being excluded), MgO , ZnO and $\text{Sn}_x\text{Zn}_y\text{O}_z$ (x and y each having a non-zero value; $z = 2x + y$), and the layers based on AlN and $\text{Si}_3\text{N}_4/\text{AlN}$ mixtures.

Preferably, the barrier layer is non-conducting. Optionally, an additional layer of SiO_2 , SiOC or Si_3N_4 different from the barrier layer may be applied to the
5 barrier layer before the first functional layer is deposited.

As examples of functional layers, mention may be made of TiO_2 anti-soiling layers and ITO, F:SnO_2 , Sb:SnO and
10 Al:ZnO conductive layers.

In accordance with another particular feature of the present invention, the alkaline-earth metal content includes barium only in a limited proportion, that is
15 to say in a quantity such that the BaO content does not exceed 2% by weight of the glass composition.

In accordance with yet another particular feature of the glass plate of the present invention, the said
20 plate has an alkali metal content under conditions that ensure what is called a "mixed alkali" effect. Preferably, the alkali metals are lithium, sodium and potassium. In particular, the alkali metals are sodium and potassium that are present in the form of their
25 corresponding oxides, Na_2O and K_2O , in molar quantities that satisfy the following relationship:
$$0.35 \leq \text{K}_2\text{O} / (\text{K}_2\text{O} + \text{Na}_2\text{O}) \leq 0.65.$$

In accordance with other particular features of the
30 glass plate according to the present invention, the said plate has an alumina weight content not exceeding 3% and/or a silica weight content not exceeding 65%.

If the glass plate has a coloration-sensitive surface
35 region, which has a composition different from that of the core with the quantity of reducing agent as defined above or is provided with a preferably non-conducting barrier layer, also as defined above, the surface layer capable of limiting or preventing the migration or

reduction of the one or more M^{n+} species advantageously has a thickness of less than 100 μm , preferably less than 50 μm and especially less than 20 μm .

5 At least in the two cases that have just been mentioned, the glass plate may be produced in the form of a ribbon obtained by the float process on a bath of molten metal, such as a bath of tin, that coloration-sensitive face of the glass in the finished product
10 being the one on the opposite side to that which was in contact with the tin.

In accordance with yet another particular feature of the glass plate according to the present invention, the
15 said plate has a lower annealing temperature, also called the strain-point temperature, corresponding to the temperature at which the glass has a viscosity of the order of $10^{14.5}$ poise, which is above 550°C , in particular above 580°C .

20 In accordance with yet another particular feature of the glass plate according to the present invention, if the said plate is produced on a bath of molten tin, its composition is chosen so as to allow it to be produced
25 under conditions that discourage the migration of Sn^{2+} or H_2 into the atmosphere face of the glass ribbon. To do this, the H_2 content of the N_2/H_2 reducing atmosphere above the bath is lowered relative to the normal working conditions, in order to decrease the SnS
30 saturation vapour pressure and to limit the diffusion of H_2 into the atmosphere face. The temperature of the bath and that of the glass are also lowered relative to the normal working conditions, the sulphate content of the glass being advantageously lowered relative to the
35 normal working conditions in order to reduce the SnS content.

In particular, at least one of the following conditions is satisfied:

- viscosity of the glass corresponding to $\log \eta = 3.5$, at a temperature not exceeding 1230°C , preferably between 1180 and 1220°C (η being expressed in dPa.s);

- 5 - temperature of the bath not exceeding 1220°C ;
 - temperature at which the glass is poured onto the bath of molten tin not exceeding 1280°C ;
 - H_2 content in the atmosphere of the bath 7% by volume or less.

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In accordance with other particular features of the glass plate according to the present invention, the said plate contains at least one element capable of colouring the glass with a colour that is complementary to the colour at risk owing to the diffusion of M^{n+} , for example Co^{2+} .

A glass having the following composition satisfies the present invention, the proportions by weight of the constituents being the following:

20	SiO_2	:	65-75%
	Al_2O_3	:	0-3%
	ZrO_2	:	2-7%
	Na_2O	:	0-8%
25	K_2O	:	2-10%
	CaO	:	3-10%
	MgO	:	0-5%
	SrO	:	3-12%
	BaO	:	0-2%
30	Other oxides	:	0-2%.

The subject of the present invention is also a process for manufacturing a coloration-resistant glass plate in a float process in which it floats on a bath of molten tin, characterized in that the float process is carried out under the following conditions:

35 - viscosity of the glass corresponding to $\log \eta = 3.5$, at a temperature not exceeding 1230°C , preferably between 1180 and 1220°C (η being expressed

in dPa.s);

- temperature of the bath not exceeding 1220°C;
- temperature at which the glass is poured onto the bath of molten tin not exceeding 1280°C;

5 - H₂ content in the atmosphere of the bath 7% by volume or less.

The present invention also relates to the application of a glass plate as defined above, or obtained by the process as defined above, to the manufacture of plate-shaped glass products that have received metal coatings liable to generate a coloration during treatments, especially at high temperature, during their manufacture and/or during use, owing to interactions between the components of the glass itself and these metals, in particular to the manufacture of emissive displays, such as plasma display panels, electroluminescent screens and field-emission displays, flat lamps, index-graded microlenses and rear windows for motor vehicles.

The following examples illustrate the present invention, without however limiting the scope thereof.

25 EXAMPLES 1 to 3

These examples illustrate the effect of the temperature at which the glass is poured and of the H₂ content in the bath of molten tin on the coloration of the final glass.

Conventional soda-lime-silicate glasses were produced in the form of a ribbon by floating on a bath of molten tin under the conditions defined below. These glasses had the chromatic coordinates L*, a* and b* given below, these being measured, for a thickness of 6 mm, under illuminant D₆₅ taking the CIE 1931 colorimetric reference observer.

	Ex. 1	Ex. 2	Ex. 3
Pour temperature (°C)	1269	1330	1330
H ₂ content (%)	6	0	> 6
L*	94.7	94.5	94.5
a*	-2.01	-2.44	-2.47
b*	5.59	6.63	7.31

This table shows that the glasses of Examples 1 and 2 according to the invention have a lower b* value than that of the glass of Example 3 (comparative example),
5 this reduction corresponding to a less pronounced yellow coloration. The lower pour temperature of the glass (Example 1) or the lower H₂ content in the bath of molten tin (Example 2) enables the yellowing of the glass to be reduced.

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EXAMPLES 4 and 5

These examples illustrate the influence of the glass composition on the surface content of reducing agent.

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A metallic silver layer about 400 nm in thickness was deposited on a glass sheet by cathode sputtering. After treatment at 600°C in air for one hour, the face bearing the silver coating was treated with nitric
20 acid.

The glass according to the invention (Example 4) had the following composition, in % by weight:

	SiO ₂	:	67.5
25	Al ₂ O ₃	:	0.5
	ZrO ₂	:	2.0
	Na ₂ O	:	4.0
	K ₂ O	:	8.0
	CaO	:	9.0
30	SrO	:	9.0.

The quantity of reducing agent, measured by SIMS as

indicated above, was 2.89×10^{-8} mol/cm². This quantity was 1.40×10^{-7} mol/cm² for a conventional soda-lime-silicate glass obtained by floating on a bath of molten tin and treated under the same conditions (Example 7).